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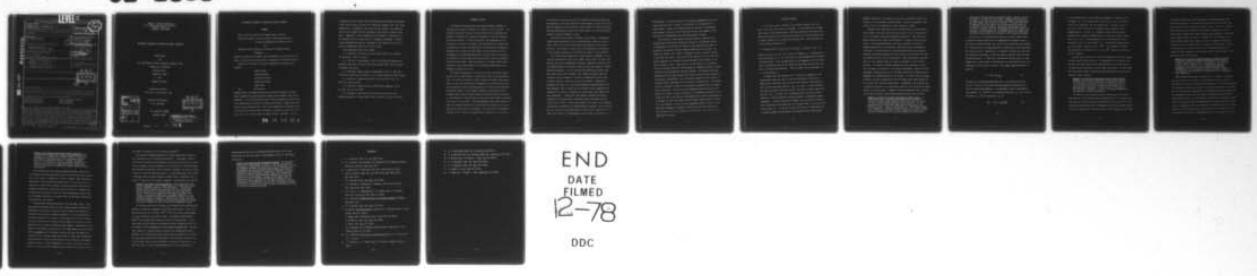

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The initial effort was to seek the origin of crystal structure determination by studies of terms in the energy of higher order than second in the pseudopotential. This study suggested the determining role of d-states and therefore led to studies of transition metals and, in the final year, to a concentration on transition-metal compounds. This report discusses the evolution and the problems addressed. The final section describes the principal findings, each topic being summarized by a paragraph on the status of that problem. The completed parts of the program have been published in the series of papers listed in the report.

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ELECTRONIC STRUCTURE OF TRANSITION METAL COMPOUNDS

Final Report

for

U.S. Army Research Office (Research Triangle Park)

Project No. P-10995-MS

Contracts Nos.

DAAG29-73-C-0024

and

DAAG29-77-C-0022

covering the period

1 May 1973 — 30 September 1978

Principal Investigator

W. A. Harrison

G.L. Report No. 2858

September 1978

ELECTRONIC STRUCTURE OF TRANSITION METAL COMPOUNDS

SUMMARY

This is the final report for research under contracts:

DAAG-29-73-C-0024 "A Critical Study of Pseudopotentials and Structure Determination in Simple Metals",

and

DAAG29-77-C-0022 "Electronic Structure of Transition Metal Compounds",

covering a period of five years, but with funding for only four of those years. (A year lapse occurred prior to approval of the second contract.)

During the four years the contract supported in succession six students:

Joseph Fields

Soloman Katzman

Christopher Ashley

Theodore Dinterman

Ralph Sokel,

and Sver Froyen.

Fields, Ashley, and Sokel have received their Ph.D. degrees, but only Sokel finished as my student and his support was from NSF at the time of completion. The initial proposal was to seek the origin of crystal structure determination by studies of terms in the energy of higher order than second in the pseudopotential. This study suggested the determining role of d-states and therefore led to studies of transition metals and, in the final year, to a concentration on transition-metal compounds. In the

following section we discuss this evolution and the problems we addressed. In the final section we describe the principal findings, each topic being summarized by a paragraph on the status of that problem. The completed parts of the program have been published in the series of papers listed below. Summaries of these findings also will appear in "The Physics of The Chemical Bond", in press with W. H. Freeman, and Company. Progress on the problems which were not completed at the termination of the contracts is summarized there also, as well as here.

Papers published under this program:

W. A. Harrison, "The Physics of the Chemical Bond," W.H. Freeman (San Francisco, 1979), in press.

W. A. Harrison, "Proceedings of the 4th International Symposium on Electronic Structure of Metals and Alloys, Gaussig, GDR, 1974; published in Dresden, GDR (1974).

W. A. Harrison, "Metal Insulator Transitions," by N. F. Mott and "Electrical Conduction in Solids," by J.P. Suchet, Review in Physics Today.

W. A. Harrison, "Bonding Properties of Ionic Solids," Bull. Am. Phys. Soc. 22, 410 (1977).

W. A. Harrison, "Angular Forces in Noble Metal Compounds," Bull. Am. Phys. Soc. 23, 16 (1978).

W. A. Harrison, "From Electronic Structure to Dielectric and Bonding Properties," invited paper, Bull. Am. Phys. Soc. 23, 406 (1978).

PROBLEMS STUDIED

The question being addressed has evolved rapidly, leading to a remarkably wide range of studies for a period of only five years. The evolution has arisen from our success in each case at answering the question at hand and the consequent appearance of the next important and central question. We have been able to take advantage of this success by a turn-over of students, (a continuing Ph.D. student must be permitted to pursue the ramification of the question he addresses, causing a time constant for refocusing of several years), and the willingness of the Army Research Office to let us seek out the important question at each stage rather than provide a specific program of activities years ahead. What we perceive as a change in this policy, reflected in the stated reasons for discontinuing AROD support, has brought the program to an end.

Our initial proposal was to explore the role in structure determination in the simple metals of third-order terms in the pseudopotential. We quickly learned that terms of fourth and higher order had an effect in structure determination comparable to the third-order terms and we therefore turned to general multi-ion interactions arising from such higher orders.[1] This brought attention to the special role of straight linear arrays of atoms within the structure and in particular to the influence of d-states above or below the Fermi energy in shifting the energy of such arrays.[1] The summing higher orders also brought to light two distinct approaches to the multiple scattering, one valid at high energy and another at low energy. The evaluation at intermediate energies will be required for quantitative comparison of the energies

of different structures but we did not undertake this specialized task. The analysis to this point appeared to have brought to light the factors which do determine the structures in these systems,[1,2] factors different from any evoked before, and in fact quite distinct from the third-order terms we initially proposed to study.

We did carry this chain of analysis a step further in seeking the longest-range interatomic forces in semiconductors, where the correct result cannot in principle be obtained from expansion in the pseudopotential. Any effects of these forces can unambiguously be detected in the vibration spectrum, so we applied the theory to this problem.[3]

The unanticipated finding that d-states played a dominant role in structure determination even in the simple metals, where for most other purposes they can be disregarded altogether, suggested a different path for research which we initiated in parallel with the analysis of pseudopotential expansions: If the d-states were dominating structure even where their effects are otherwise weak, perhaps we should study the transition metals themselves — systems of considerably greater technological interest — where the effects are stronger. Comparison of treatments in terms of our own transition-metal pseudopotentials[4] and LCAO expansion, akin to those used in covalent solids, suggested that though both are valid in principle the latter might prove simpler and more perspicuous. Indeed this LCAO approach becomes particularly tractable in transition-metal compounds in which the bands are completely full or empty. We have thus begun on the theory of the bonding and dielectric properties of transition-metal compounds. The particular path has led us to an approach which we believe gives immediate new insight and a context for addressing the entire range of properties of

these systems. We would anticipate this approach expanding back into the transition metals and it could, if one desired, be continued back to simple metals. However, the simple metals are systems of considerably less interest, selected in the first place because they seemed to offer more hope for understanding than the more important systems.

The evolution of this program is quite unique in starting from a problem selected for purely theoretical reasons as the simplest system to understand, and drifting for reasons of pure scientific necessity to systems of successively greater technical importance to the Army. One might have thought this a happy circumstance but for incidental reasons it has been the reverse. The evolution has brought us to the transition-metal compounds with insights arising principally from analysis of the other systems en route. This places us in the context of an extensive group of technical people who leap-frogged the elementary systems in order to study the technologically important systems. Of necessity they have developed views of these systems which correlate the various properties of this system, representing a very considerable progress in the science of transition-metal compounds, but along quite a different path. The results of such a scientist's review of the proposed continuation of our program may be inevitable. He can note the outstanding track record of our research, but lament a lack of citations to the extensive literature on the subject and wish a more detailed documentation as to what calculations are to be done. He may also object that the "double oxide", which I believe to be the simplest to treat, is more complicated from his point of view than other compounds. Acceding to these objections would destroy the very features which have given us our "outstanding track record" and we choose not to do that.

PRINCIPAL RESULTS

A very major advance, relative to the initial proposal, was made prior to the time the contract was awarded. It was found that the higher order terms in the pseudopotential, which had previously been almost universally discarded, led to many-body forces which at large distances were of simple enough form to be explicitly written down. The resulting form of the n-body interactions is[1]

$$V \propto \Sigma(E_F/k_F)(\lambda/k_F)^n \cos k_F(\ell_1+\ell_2+\ldots\ell_n)/[\ell_1\ell_2\ldots\ell_n(\ell_1+\ell_2+\ldots\ell_n)] \quad (1)$$

where the sum is over all closed paths, of segments ℓ_i, connecting the n ions in question and λ is of the order of the pseudopotential divided by the Fermi energy. This led immediately to the suggestion that the alignment of neighboring ions and the energy of the nearest d-states were central to structure determination. (This followed from the dependence of λ on path geometry.)

We began under the program (with J. Fields) the summation of the interactions among such rows of atoms and discovered collections of higher order terms which could be given clear physical interpretations. One, clearly appropriate when the $k_F\ell_i$ are large, is simple kinematic electron scatterings from atom-to-atom. The second, clearly appropriate when the $k_F\ell_i$ are small, is a renormalization of the electron wavenumber as it moves through an "effective medium" of background pseudopotentials. A third, which may be thought of as the effect of successive scatterings by the same atom, is the phase shift of the oscillatory factor in Eq. (1). A study of the last two effects in combination (by C. Ashley) showed that the effect of the phase shift on the nearest-

neighbor interaction, for example, could even be reversed in sign by the inclusion of the wavenumber renormalization. Clearly a systematic formulation of all of the higher-order terms together is needed.

Precisely these same three effects are essential to the interpretation of EXAFS, the x-ray studies of local atomic structure being carried out at the Stanford Synchrotron Radiation Laboratory. Both Fields and Ashley continued their study with Professor S. Doniach on this interpretation. In the meantime Bertoni, Bortolani, Calandra, and Nizzoli[5] examined specifically the three-body contribution from the kinematical scattering in connection with the vibration spectrum of the hcp metals, finding it explained anomalous vibration spectra for beryllium,[6] but gave only smaller effects for the heavy metals. These results were consistent with, but more complete than, our study (S. Katzman) of the vibration spectrum. In addition, Professor Marshal Pound has proceeded to study, with a student, the effects of the second two phenomena (phase shift and wavenumber renormalization) on the two-body interaction in metals using a semiempirical parameterization of the effects. It would be quite straightforward to proceed systematically with the higher-order terms though this is a rather major long-term undertaking. Furthermore, even assuming that it would be successful in a quantitative theory of the structures of simple metals, our starting goal, I judged it much less important than following up the other technical opportunities which had arisen from the study.

> Summary of status of the multi-ion theory of simple metals: It still appears that the second-order theory which is generally believed to explain simple-metal structures does not even contain the features which really determine those structures. We still believe the full higher-order theory would though this is not known for certain. (Note, in particular, the "unsettling thought" in the summary of semiconductor interactions.) Our analysis showed that a particular selection of terms (third-order, d-state contribution) correlated with all cubic and hexagonal structures and

axial ratios for monovalent and divalent metals. However, we have no reason to believe that the effects of higher multi-ion forces are smaller, nor that the phase shifts, wavenumber renormalization, and other higher order effects are smaller. It is not clear that exploration of any one feature gets us further and we choose not to undertake the full problem. Concerning other properties than structure, it appears that the traditional second-order theory[7] of the entire vibration spectrum — and perhaps all other nonstructural problems — may be adequate for the heavier metals, but significant third-order corrections may be needed for the lithium-row elements.

Our study of the pseudopotential theory of covalent solids[8] under a different program showed that the pseudopotential expansion itself is not valid in covalent solids; thus, even if one carried the above analysis out to all orders in the pseudopotential it would lead to the wrong answer for covalent solids. Nonetheless it is possible to define and calculate the long-range interatomic interactions using a different basis (valence-band Bloch states). R. Sokel and I carried this through under our AROD program with a result which is interesting in its own right as well as in comparison with the result in metals. The longest-range interaction is given by[3]

$$U \propto \lambda^2 E_F \exp(-k_g r) \qquad (2)$$

for the case of direct-gap semiconductors. (An oscillatory factor, $\cos \vec{q}_o \cdot \vec{r}$ enters if the conduction-band minimum is displaced by $\vec{q}_o$ from the valence-band maximum.) The exponential decay is described by the parameter k_g related to the conduction-band mass m_c, the valence-band mass m_v, and the energy gap E_g by

$$k_g^2 = 2(m_c + m_v) E_g/\hbar^2 \qquad (3)$$

It is interesting that this "imaginary wavenumber" is related to the wavenumber k_F in the simple-metal interaction, Eq. (1), by continuation of the wavenumber into the complex plane. However, we may see that this result could never be obtained from an expansion in the pseudopotential: the gap E_g ultimately arises from the pseudopotential and is directly proportional to a particular Fourier component of it, W_1.[8] The interatomic forces are proportional to the derivative of Eq. (2) with respect to r and therefore proportional to k_g and finally, using Eq. (3), to $W_1^{1/2}$. The expansion in pseudopotential gives an expansion in W_1, and $W_1^{1/2}$ cannot be written as such an expansion.

We used this interaction to study the vibration spectrum of various covalent solids[3] and found that it is responsible for a familiar flattening of the transverse acoustic spectrum which is the only feature of the spectrum not duplicated by short-range force models. We thus showed that long range coulomb interactions (bond-charge effects) are not important in these systems.

> Summary of the status of long-range interactions in semiconductors: The vibration spectrum of covalent solids appears to be describable entirely in terms of pseudopotentials but the long-range interactions differ in a qualitative way from those in metals and cannot in principle be obtained from a pseudopotential expansion. If these effects of "covalency" have an effect in metals, it will not be obtained through such an expansion, an unsettling thought.

The effects of the d-states had been incorporated in our simple metal theory[1] using transition-metal pseudopotentials.[4] Following this lead into the transition metals, we explored the band structure in LCAO terms and discovered that use of sd-hybrids allowed a reasonable description of the energy bands with only three or four parameters, rather than

the eleven required in earlier treatments of d-bands hybridized with free-electron bands.[9] The reason this could be done was the same that such a reduction could be made in covalent solids: the use of directed hybrids gave a natural suggestion as to which combinations of interatomic matrix elements were large and which were negligible. We carried this through both for bcc and fcc structures.[10] The resulting interatomic matrix elements vary slowly over the 3d-transition series and provide an ideal starting point for the study of these metals. However, we postponed such a study in favor of the corresponding prospect for transition metal compounds which are more simply treated because of the absence of partly-filled bands.

Summary of the status of bonding theory in transition metals: We have put together a summary of existing theory by earlier workers[10] and the hybrid theory outlined here. The bringing of this together appears to be an outstanding scientific opportunity, but one which can be temporarily postponed. Parameters can better be selected when the Moruzzi, Janak, and Williams[11] calculations are available and after experience is obtained in the calculation of properties of the transition-metal compounds.

There existed energy-band calculations for a number of compounds, and in fact LCAO fits to them, so we undertook to develop methods for calculation of properties from the LCAO parameters. Such methods existed for tetrahedral solids, which could be treated bond-by-bond. Properties such as the dielectric susceptibility are dominated by the distortion of such independent bonds, with only small contributions from transfer of charge between bonds. It has, however, recently been convincingly shown[12] that in the alkali halides the susceptibility is *not* dominated by distortions of independent ions, as has been the traditional view, but is dominated by transfer between ions. Thus the covalent techniques could not be carried over directly to the alkali halides, nor presumably to ionic

transition-metal compounds. We set out to carefully reformulate the calculation of properties for such systems.

This came during the year when the first three-year contract had run out and we were waiting for the final one-year extension. The work was therefore supported on my NSF grant and directed at simple ionic compounds. We proceeded from a basis of independent ionic states and included interatomic matrix elements by perturbation theory. For dielectric properties these matrix elements "softened" the ionic charges, reducing them by about 40% in all alkali halides. The charge redistribution under an applied electric field could then be directly calculated by a slight extension of the softening calculation and gave a reasonably quantitative account of the susceptibilities of the alkali halides which did not depend upon any experimental information about the alkali halides except the crystal structure and composition. We also obtained the charge redistribution under displacement of the ions and therefore the effective transverse charge giving coupling of the vibrations to the infrared and the static dielectric constant, both in good accord with experiment and without additional experimental input. The calculation of bonding properties was also interesting and surprising. There is a second-order contribution to the bonding but we showed it to consist entirely of radial forces. The angular rigidity which we usually associate with bonding arises only in fourth order; it is a small independent physical effect which we called the "chemical grip" to distinguish it from the principal bonding term which is radial.

These studies under NSF support provided a new, elementary, first-principles theory of the simple ionic compounds and provided the basis for a study of transition-metal compounds once the program started again. We

began with noble-metal halides as the simplest extension of the alkali halide systems, and one in which there appeared to be a great reduction in angular due to the noble-metal d-band. (See for example the plot of experimental rigidities in Harrison and Phillips[13] in which the CuCl point appears quite anomalous.) The analysis was disappointing, but therefore also quite informative. The chemical grip turned out not to play a role since it is associated with the coupling between occupied states on one atom and empty states on the other. Here all the valence states on the halide are occupied and so are the noble-metal d-states. It was therefore necessary to invoke coupling between the d-states and the empty s-states on the same ion. (No contributions to bonding can arise from coupling between full states, as with two interacting inert gas atoms, nor between two empty states.) This intra-atomic coupling is more appropriately called ion distortion and it indeed reduces the angular rigidity. However, quantitative studies of the coupling through crystal-field splitting (by Froyen) showed that it was quite negligible. A subsequent treatment (by Froyen) of a higher-order coupling through the neighbors (a fourth-order term) gave a larger contribution but still one small on the scale of the discrepancy we believed existed. Froyen then reexamined the evidence for an anomalous reduction in rigidity and found it quite unconvincing. The most recent measurements of angular rigidity did give larger discrepancies in the sp-theory for noble-metal halides, but not significantly larger than would be estimated by extrapolating the discrepancies from the isoelectronic series of compounds of increasing valence.

Status of the theory of noble-metal halide rigidities: We conclude that bonding theory based upon sp-bond orbitals is adequate for the noble metal halides, though the theory as performed has increasing errors with increasing polarity — worst for the noble-metal halides. However, the direct effect of the d-states is small and probably in general we can restrict attention to interatomic matrix elements and directly estimate any ion-distortion effects from the fourth-order theory.

We considered also the transition-metal monoxides, which are in the rocksalt structure and might seem to be the next most direct extension of the theory of simple ionic solids. However, these systems are dominated by electron-electron interactions (this has been known for some time; a rather recent analysis is given by Koiller and Falicov[14]) throwing a theoretical uncertainty into the problem. In addition the d-states may be expected to have only small experimental effects (just as the chemical grip had only a small effect in the alkali halides) so they would be a poor choice.

The perovskite structures appeared to be the ideal choice. They show well-defined bands which have been reliably given by Mattheiss.[15] Furthermore, we wished to learn the relation between the stability of the open structures with octahedral neighbors to the transition-metal ion and the presence of d-states. We had shown earlier in the program that the d-states did not stabilize the octahedral structure as a naive application of the idea of sd-hybrids would suggest. Application of the theory of the chemical grip theory at this stage showed that the d-states tend to destabilize the octahedral structure and that the addition of electrons to the conduction band only serves to reduce this destabilization but does not "blow up the structure" like a balloon as had seemed plausible before a careful formulation. We then calculated the contribution of the electrostatic energy to the rigidity and found that it was

the source of stability, as in the alkali halides.[10]

The next two problems appropriate to these systems are the dielectric properties and the vibrational properties. I had begun a study of the dielectric properties and Froyen was following through when we learned that the program is being terminated so he has shifted to the NSF program. The vibrational properties also are directly tractible, in this case using a model of localized vibrational modes in a simple molecular lattice which I developed under the AROD program but applied only to amorphous SiO_2 as a test.[10] This also is too large a program to initiate this near the end.

> Status of the theory of the perovskites: The minimal basis LCAO theory, analogous to that of simple solids but containing d-states, gives a reasonable account of the known bands.[15] The nearest-neighbor matrix elements extracted from the fit to these bands can be used directly in the calculation of properties using a direct extension of the approach we developed for simple ionic solids. Such analysis showed that the angular stability of the octahedral structure arises from electrostatic effects, not from effects analogous to covalency. There is every reason to believe the direct extension to dielectric properties and effective charges will also be useful but this is only in the preliminary stages.

At the same time we were exploring the perovskites we initiated some studies of conducting compounds such as Nb_3Sn, NbN, and WC. There exist band calculations for the first two[16,17] which are readily interpretable as in the perovskites in terms of LCAOs. The familiar Labbé-Friedel model[18] of the Nb_3Sn band structure is such an interpretation. In the last weeks we have focussed our attention on these systems which will be of interest in the superconducting and catalytic programs here. We, however, remain at a learning stage in which we are finding which matrix elements can be discarded and what values should be taken for the others. The next stage should be the calculation of the electronic structure in a sufficiently simple form to allow the calculation of properties. Perhaps the science of these systems would be most rapidly advanced by

addressing the dielectric and bonding properties first, but circumstances may dictate that these be leap-frogged in favor of the surface properties.

Status of the theory of metal-metalloid systems: The electronic structure for some systems is known,[16,17] but has not yet been sufficiently parameterized (as it has in the perovskites) to allow the immediate treatment of properties; because of the partially filled bands they are intrinsically more complicated than the perovskites; and formulation of properties (dielectric constant, effective transverse charge, chemical grip, local vibrational modes) which we have made under this program are not directly applicable to these systems. However, we may expect that the general approach of reducing the electronic structure to the essentials, using parameters from the known electronic structure, and detailed first-principles calculation of properties of interest should be successful for these systems as indications are that it is for the simpler perovskites.

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